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## PHASE CHARACTERISTICS IN TECHNOLOGY OF MATERIALS BASED ON DISPERSE SILICATE SYSTEMS

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Phase characteristics are considered for the technology of materials based on disperse systems, which makes it possible to clearly represent the process of transformation of the structure throughout the total technological cycle and to determine the required level and the method for influencing a system for the purpose of optimum implementation of a particular stage or operation to ensure the formation of the optimum structure and to obtain end products with preset properties.

The process of producing materials based on disperse systems (S + L + G) consists of four main stages: preparation of the initial disperse system (the molding mixture, slip, or suspension in the course of crushing, fine milling, and mixing), imparting the required shape to it (casting, plastic molding, compression), transforming the coagulation system into a condensation system (drying, removal of the temporary binder) and then to the crystallization structure (firing).

The technological convenience implies the successive transformation of a structure with a low level of organization and strength into a structure of higher order and strength. Such transformation of structures can be implemented under the isolated or combined effect of the following five energy factors, which can be arbitrarily split into two groups:

- external energy factors: thermal, mechanical, and electrochemical, or electrophysical;
- internal energy factors: the chemical potential of the system and its free surface energy.

The main specific feature of disperse systems is their extended interphase surface and hence a substantial excess in the Gibbs surface energy. The strength and level of structural organization are determined by the contact forces between the solid phase particles and the thermodynamic stability of the system.

A decrease in the interphase surface by increasing the volume of the solid phase and modifying the surface of particles and the type of contact between the particles makes it possible to increase the contact forces and transform the system or structure into a more stable state.

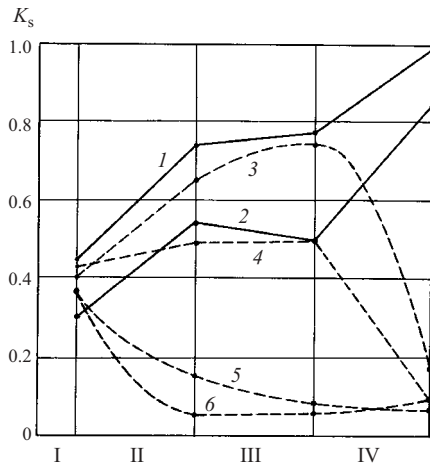
Any stage in the technology of materials based on disperse systems is accompanied by one or several physicochemical processes, which is a typical characteristic of this technology. Therefore, successive formation of structures is

based on a strictly measured effect of external energy factors on the internal energy and physicochemical properties of the disperse system, which predetermines the intensity of the main physicochemical process at a particular technological stage. Therefore, the main problem in structure formation in materials based on disperse systems is to optimize the processes of transformation of structures at all technological stages.

It is convenient to use volume phase parameters as the optimization criteria, as they reflect the most general properties of disperse systems, regardless of the type of structure, the technological stage, or the type of energy effect on the system. This primarily refers to the volume part of the solid phase  $K_s$  normalized with respect to variation within the limits of (0 – 1) or (0 – 100%) that is present in the system during the whole process. The use of  $K_s$  allows for a graphic representation of the route of reaching the preset goal in all stages of the process.

With respect to the technology of ceramics, this route can be represented as follows (Fig. 1). The initial disperse system in the form of a molding mixture, molding power, or slip ( $K_{s1} = 0.30 - 0.45$ ) in molding becomes compacted and acquires new structural characteristics ( $K_{s2} = 0.55 - 0.75$ ), which, in turn, are the initial parameters for the formation of the condensation structure (drying). The properties of molded articles and the drying conditions predetermine the behavior of the material in drying and the final parameters of the condensation structure ( $K_{s3} = 0.50 - 0.78$ ). In firing, a crystallization structure with a rather high relative density ( $K_{s4} = 0.85 - 1.00$ ) is formed, which characterizes the final parameters and the level of reaching the preset goal. Due to the diversity of materials used in ceramic production and their specific properties, the variation limits of  $K_s$  indicated in Fig. 1 are rather approximate and the route of variation of  $K_s$  can be diverse.

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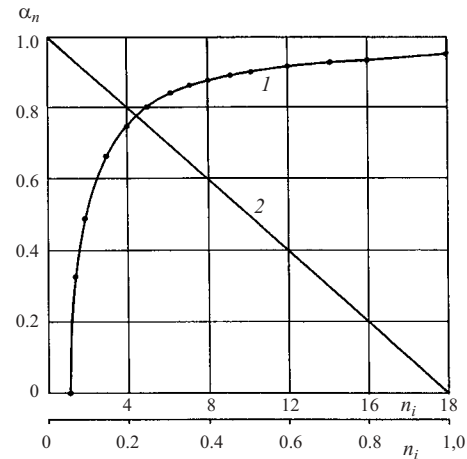
**Fig. 1.** Volume content of the solid phase  $K_s$  in different stages of producing compact ceramics (1, 2), claydite (3), foam glass (4), and porous ceramics (5, 6). Technological stages: I) preparation of disperse system; II) molding; III and IV) formation of the condensation and crystallization structures, respectively.

A similar variation route of  $K_s$  can be constructed for the process of production of porous materials. For instance, in the technology of claydite production, the initial molding mixture with  $K_{s1} = 0.38 - 0.42$  (Fig. 1, curve 3) is compacted in a screw press, granulated ( $K_{s2} = 0.63 - 0.68$ ), and dried ( $K_{s3} = 0.68 - 0.76$ ). A powerful thermal effect on dry granules in firing stimulates the physicochemical processes of sintering and swelling of the granules, when the ratio between the solid and the gaseous phases in the system significantly changes ( $K_{s4} = 0.12 - 0.18$ ). Such a curve with an extremum is typical of structure formation in porous ceramics using burning-out additives.

The use of foam- and gas-forming agents in the production of porous ceramics modifies the shape of the curve and the value  $K_s$  in structure formation usually keeps decreasing throughout the process (Fig. 1, curve 5) or, in some cases, may insignificantly increase in firing (Fig. 1, curve 6).

The variation curve of  $K_s$  in the production of foam glass has a peculiar shape. The initial finely milled batch consisting of milled glass and a gas-forming agent ( $K_{s1} = 0.43 - 0.45$ ) is placed in foaming molds and compacted ( $K_{s2} = 0.50 - 0.53$ ). This state persists in heating up to the foaming temperature, since the drying process has no effect on the phase ratio in a freely disperse system (S + G). Only after reaching the foaming temperature do the physicochemical foam-formation processes start within the system and result in a substantial modification of the volume phase composition ( $K_{s4} = 0.06 - 0.10$ ).

Thus, the attainment of a preset technological goal is the interdependent modification of  $K_s$  in various stages. If the purpose is to obtain dense materials,  $K_s$  should increase at all technological stages. If the purpose is to produce porous materials,  $K_s$  should continuously decrease or change according to an extremum dependence.



**Fig. 2.** Relationship between the degree of modification of the structure  $\alpha_n$  and the parameter  $n$ : 1) condensation of system ( $n_i = 1 - 18$ ); 2) expansion of system ( $n_i = 0 - 1$ ).

It was earlier [1] observed that the modification of the structure at particular technology stages can be estimated using the structure-energy parameter:

$$n = \frac{K_{s2} / P_2}{K_{s1} / P_1},$$

where  $P_1$  and  $P_2$  are the material porosity at the beginning and end of the process.

Valuable information on restructuring of the structure can be obtained by normalizing the value of parameter  $n$  within the limits from 0 to 1.

In compaction of the system  $n > 1$ , we have

$$\alpha_n = \frac{n_i - n_1}{n_i} = \frac{n_i - 1}{n_i},$$

where  $\alpha_n$  is the degree of rearrangement of the structure;  $n_i$  and  $n_1$  are the current and initial ( $n_1 = 1$ ) values of the parameter  $n$ .

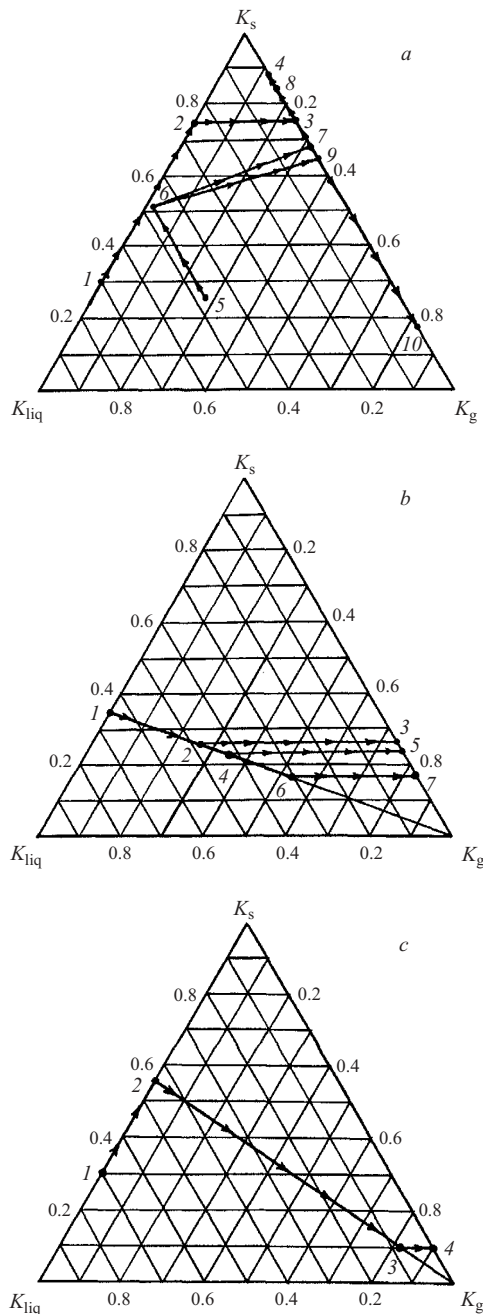
In expansion of the system  $n < 1$ , we have

$$\alpha_n = 1 - n_i.$$

It follows from the dependence  $\alpha_n = f(n)$  for a condensing system (Fig. 2) that the most intense modification of the structure occurs when the parameter varies within the limits of  $n = 1 - 6$  ( $\alpha_n = 0 - 0.833$ ). Typically, when  $n = 2$ ,  $\alpha_n = 0.5$  (or 50%). An increase in the parameter ( $n > 6$ ) is accompanied by a monotonic increase in  $\alpha_n$ .

For an expanding system, the dependence  $\alpha_n = f(n)$  is linear and true at  $n_i = 0 - 1$ .

The normability of the parameter  $n$  variation makes it possible to use the values of  $n$  and  $\alpha_n$  as the characteristics of the degree of transformation of the structure in kinetic studies of processes occurring at different technological stages.



**Fig. 3.** Phase diagrams of production technologies: *a*) ceramics produced by slip casting (1–2–3–4), ceramic brick (5–6–7–8) and claydite (5–6–9–10); *b*) foam ceramics; *c*) foam silicate based on sodium silicate solution.

Furthermore, the parameters  $n$  and  $\alpha_n$  allow for a quantitative estimation of the structure-forming process dynamics taking

into account the intensity of the external or internal energy impact on the system. With respect to the technologies considered (Fig. 1), the formation of the material structure in different stages can be estimated using the parameters listed in Table 1.

The use of the only parameter  $K_s$  that reflects the degree of approaching the absolutely compact state of the system is insufficient for characterizing the process based on the proposed model. One can obtain more illustrative information on modification of structures based on the law of constancy of the volume phase composition of disperse systems, which holds that the sum of the volume parts of the solid, liquid, and gaseous phases in a system is a constant value at any given moment regardless of the type of the structure, the technology stage, or the type of energy impact on the system.

According to this law [1], single technology stages can be plotted as a phase diagram in a triple coordinate system ( $K_s - K_{liq} - K_g$ ). By summing the phase diagrams of individual process stages, it is possible to develop the phase characteristic of the whole technological process, which represents interdependent modification of the volume phase composition of disperse structures transformed under the effect of external energy impacts.

Figure 3 shows diagrams typical for ceramic technologies based on Rodionovskoe clay including slip casting, ceramic brick, and claydite, as well as foam ceramics using gas- and foam-forming agents and foam-silicate materials based on sodium silicate solution (liquid glass). The variations of the phase composition of the ceramic mixture and slip based on Rodionovskoe clay in molding and drying were analyzed in detail earlier [1]. The phase composition of the dehydrated clay mixture (point 7) and slip (point 3) is located along the line  $K_s - K_g$ . The effect of high temperature (1050°C) for 1 h on this material leads to a regular but disproportionate increase in the values of  $K_s$ . Introduction of 4 wt.% mazut (fuel oil) into the clay mixture in the production of claydite has virtually no effect on the phase composition of the mixture in condensation (line 5–6) and somewhat lowers  $K_s$  in drying (point 9). Subsequent firing of samples for 0.5 h at 1200°C modifies the phase composition of the material (line 9–10) and converts it to a qualitatively different highly porous state.

The initial phase composition of the suspension used in the production of foam ceramics is positioned on line  $K_s - K_{liq}$  and is characterized by  $K_s = 0.32 - 0.36$ . The content of the solid phase provides for required flow properties of the suspension and its stability in pororizing. The addition of gas- and foam-forming agents increases the content of the

**TABLE 1**

Technological stage	Ceramics				Claydite				Foam glass			
	$K_{s1}$	$K_{s2}$	$n$	$\alpha_n$	$K_{s1}$	$K_{s2}$	$n$	$\alpha_n$	$K_{s1}$	$K_{s2}$	$n$	$\alpha_n$
Condensation	0.45	0.75	3.66	0.73	0.42	0.68	2.93	0.66	0.45	0.53	1.37	0.27
Drying	0.75	0.78	1.18	0.15	0.68	0.72	1.21	0.17	0.53	0.53	1.00	0.00
Firing	0.78	0.99	27.9	0.96	0.72	0.12	0.05	0.95	0.53	0.10	0.09	0.90

gaseous phase and modifies the phase composition of the system, which evolves along line  $1 - K_g$  connecting the initial composition (point 1) with the concentration triangle apex  $K_g$ . In pore formation the initial system acquires certain geometrical dimensions and, depending on the quantity of the emitted or involved gaseous phase, the variation in the sizes of the system may stop at points 2, 4, or 6 with the corresponding densities of material in these points, whereas  $\rho_2 > \rho_4 > \rho_6$ .

A further modification of the phase composition of the system occurs due to the removal of moisture from the material and evolves with  $K_s = \text{const}$  along the lines 2–3, 4–5, and 6–7 until the system reaches the two-phase (S + G) state. By selecting a particular firing mode for dried articles and using different additives, it is possible to control the phase composition of the finished product, which will be located as well on the line  $K_s - K_g$ . The resulting phase characteristics can be used for calculation and design of the phase composition of the initial suspension and the target product, for instance, foam ceramics, as well as for controlling the process of pororizing of the suspension.

In a similar way, the phase characteristics can be used in the production of foam silicate based on sodium silicate solution. The phase composition of the initial sodium silicate solution with silicate modulus  $m = 3$  and density of 1450 kg/m<sup>3</sup> correlates with point 1 on line  $K_{\text{liq}} - K_s$  and contains 30% solid phase ( $K_s = 0.30$ ).

Foaming of sodium silicate solution of this composition involves significant consumption of heat and instability of the process. The application of special techniques (introduction of finely milled mineral fillers, additional drying, etc.) makes it possible to increase the solid phase content in the initial system to  $K_s = 0.50 - 0.57$  (point 2). A specific feature in producing foam silicate based on sodium silicate solution is the necessity of a thermal effect on the initial system at temperatures of 350–500°C. At the same time, free water is intensely removed and fixed water participates in pororizing of the system, whose phase composition varies along line 2–3–4, whereas line 2–3 lies on the segment connecting the initial composition (point 2) with the triangle vertex  $K_g$ . Foaming of the material due to vapor formation stops at

point 3 and a further modification of the phase composition occurs with  $K_s = \text{const}$  along line 3–4. The production of foam silicate with a volume mass of 50–300 kg/m<sup>3</sup> ( $K_s = 0.02 - 0.12$ ) depends on the coordinates of point 3, and the possibility of its maximum approximation to the vertex of triangle  $K_g$  depends on the phase, chemical, and mineral composition of the initial mixture, as well as the mode of the thermal effect upon the system.

Thus, effective control of structure transformation processes and optimum organization of technological operations can be implemented by satisfying the law of constancy of the volume phase composition of the disperse system and the principle of technological coordination between the rate of change of the structural characteristics of the system and the rate of the physicochemical processes accompanying the particular technological operation.

The production of materials with preset properties requires the maximum use of the possibilities of the physicochemical processes and developing normal conditions for them to ensure the formation of structure in a direction beneficial for accomplishing the final technological target. It is possible to control the intensity and direction of a physicochemical process by varying the conditions of the technological operation or by using modifier additives capable of intensifying or weakening the effect of the physicochemical process on the particular technological operation or stage.

The use of phase characteristics in the technology of materials based on disperse systems makes it possible to represent in a pictorial form the transformation of structures throughout the technological cycle and to identify the required level and method of influencing the system for the purpose of the optimum implementation of the particular stage or operation that ensures the formation of the optimum structure and the production of the final product with the prescribed properties.

## REFERENCES

1. V. A. Lotov, "Control of the structure-formation process in the technology of ceramic and silicate materials," *Steklo Keram.*, No. 5, 21–22 (1999).